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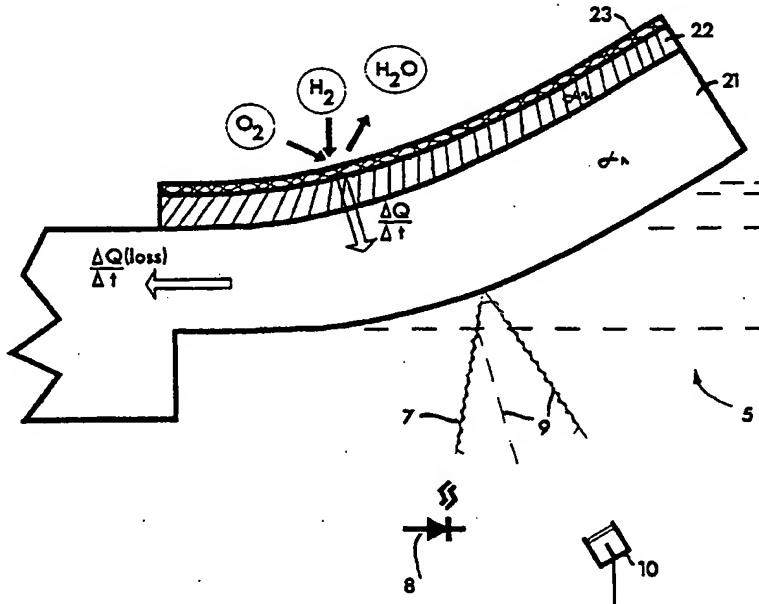
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(54) Title: CALORIMETRIC SENSOR

(57) Abstract

A calorimetric sensor is described, in which a bimetallic lever (21, 22) is combined with a chemical sensing layer (23), e.g. a catalyst, and a sensitive device (6) to determine any deflection of the bimetallic lever. Due to its high sensitivity, the new sensor is applicable in various technical fields.



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DESCRIPTION

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Calorimetric Sensor

The invention relates to a calorimetric sensor. Specifically, it pertains to a calorimetric gas sensor. A calorimetric gas sensor measures gas concentrations as a function of the temperature change produced by the heat 10 of an reaction on its surface covered by a chemical sensing layer, in particular by a catalyst.

BACKGROUND OF THE INVENTION

15 The technical field of the invention are calorimetric sensors. The known calorimetric sensors are produced by combining a sensitive calorimeter, a catalytic surface, and, if necessary, a heater to maintain the catalyst at a desired operating temperature.

Most commonly, the calorimeter is a thermo-electric transducer converting the 20 thermal signal into an electrical signal. It is commonly known to use a thermocouple or a resistance thermometer as such a transducer. The simplest known form of a catalytic gas sensor is a simple platinum coil. The platinum coil is able to act, both, as a heater and as a temperature sensor. Platinum also serves as an active catalyst for reactions like the hydrocarbon 25 oxidation.

Also the platinum coil sensor might still be used in spot reading instruments, it is not well suited for use in continuous operation due to a degradation of the catalyst. Improvement have been made by using more active catalysts, such as porous platinum, porous rhodium, or palladium (oxide) finely 30 dispersed in thorium dioxide (thoria), and the like. Microcalorimeters based on these materials are also known as pellistors. A detailed description of catalytic gas sensors can be found, for example, in GB-A-1501888. However,

1 the known calorimetric gas sensor is used mostly as a quantitative device for
the measurement of gases at high concentrations, e.g. as to detect an
explosive gas mixture. The sensitivity of the known devices is limited to the
range above 100 ppm. This is not enough to exploit these devices in fields
5 which require a sensitivity for traces of a gas, as, for example, in toxicologic
applications.

A higher sensitivity is achieved by a class of gas sensors known as
metal-oxide gas sensors. Metal-oxide gas sensors are based on the electrical
conductivity changes induced in a layer of metal oxide by gas adsorption on
10 its surface. Mostly, inorganic materials such as oxides of tin and zinc are
employed as sensing layers. Metal-oxide gas sensors are applied, for
example, for monitoring the exhaust gases from internal combustion engines
with a view to control the air/fuel ratio. As inorganic materials usually have to
15 be operated at elevated temperatures, considerable efforts are known to
exploit the properties of organic materials. These efforts are concentrated on
phthalocyanine and porphyrin based materials containing different metal ions.
It is an object of the invention to introduce a new calorimetric sensor. In
particular, it is an object of the invention to enhance the sensitivity of the
known sensors based on calorimetric principles. A further object of the
20 invention is to develop a calorimetric gas sensor suitable for the trace
analysis of gas mixtures. Yet another object of the invention is to supply a
miniaturized calorimetric gas sensor designed for an integrated circuitry,
especially in the form of arrays of such sensors.

25

SUMMARY OF THE INVENTION

The new catalytic gas sensor comprises a flexible element with a least two
layers of material having a different thermal expansion coefficient and one of
30 said layers or another layer able to act as chemical sensing layer, and means
to detect the deflection of said flexible element.

1 The new sensor is based on what is commonly known as bimetal or
thermobimetal effect. Bimetal switches have found a wide spread application
in many devices, though being more and more replaced by electronic devices.
In principle, a bimetallic temperature sensor is made of two tightly bonded
5 layers of materials differing in their respective thermal expansion coefficient.
These materials do not necessarily have to be metals. Therefore, the term
"bimorph" is used as a less known but more precise synonym for "bimetallic".
In case of a temperature change, both material elongate by different amounts,
thus, introducing a bending or deflection of the flexible element from its
10 original shape or position. In a first approximation, the bending radius of a
thin bimorph strip is given by $R = l/(\alpha_1 - \alpha_2)\Delta T$ with l being the length of the
strip, α_1, α_2 being the respective thermal expansion coefficients of the two
bonded materials, and ΔT being the temperature difference. The known
15 bimetallic devices, however, have sizes within the centimeter range, making
them unacceptable for any use besides a crude temperature measurement.
No bimetallic device is known which is combined with a chemical sensing
layer and able to detect a chemical reaction involving said layer.
Though the invention makes use of the bimetallic effect, the dimensions of the
new device are reduced to below one millimeter, reducing simultaneously the
20 thermal capacity and the heat flow out of the device and, thus, enhancing the
sensitivity of the device.

As for the materials, themselves, there are, in principle, no constraints upon
the shape of the flexible element used in the new device. However, to
enhance sensitivity, it has preferably a beamlike shape or is formed like a
25 triangle with a punched central portion, in which the length surmounts the
width by approximately a factor of 10. Calculations based on the simple case
of a beam as flexible element show that an optimum sensitivity can be
achieved by using long thin beams. However, thermally induced noise makes
it desirable to utilize a flexible element with a spring constant of above 1 N
30 m^{-1} and a high resonance frequency. These conditions, together with a
demand for a fast response time, enable a skilled person to optimize the new
sensor in accordance with any imposed requirement.

1 A further enhancement of the sensitivity of the flexible element can be
achieved by using more refined designs, e.g. by separating the two layers
with different expansion coefficients leaving only at a few points bridges as a
connection. However, these flexible elements have to be prepared with higher
5 accuracy than the simple elements described above. As the silicon
technology is the most developed technology for producing miniaturized
devices, it is of advantage to use materials based on silicon for the
preparation of the bimorph flexible elements. For example, Petersen
describes in the IEEE Transactions on Electron Devices, Vol.ED-25, No.10,
10 October 1978, pp. 1241-1250, the preparation of metal coated cantilevers on
silicon wafers. From other sources, the preparation of beams of SiN by
anisotropic chemical etching is known. Other feasible methods for preparing
the desired flexible element are focussed beam techniques, reactive ion
etching, and x-ray or synchrotron lithography in combination with galvano- or
15 electroforming.

The second layer has advantageously a thermal expansion coefficient α_2
which differs substantially from the thermal expansion coefficient α_1 of the
main material of the flexible element. Suitable materials are, for example,
metals like Al and Au, which are easily applicable onto the surface of Si and
20 SiN.

To make the bimorph or "bimetallic" element a tool for monitoring even small
amounts of gases, the means to detect the deflection of this element has to be
very sensitive. Several accurate methods to detect the bending of a cantilever
are known from the field of atomic force microscopy (AFM). The AFM is
25 known as a device to examine the roughness of a surface. For that purpose, a
cantilever is applied with a microscopic tip and scanned across the surface to
be examined. It is found that the methods applied in AFM to detect the
deflection of the cantilever can be advantageously employed in the new
device. With the help of these methods, lever deflections of the order of less
30 than 1 nm can be easily detected. In addition, motions of the lever ranging
from 0.001 nm up to 100 μm can be monitored, giving the new sensor a
possible dynamic range of 10^9 . It is well within the scope of an averaged

1 skilled person to choose one of the available methods known in the field of
atomic force microscopy as means to detect the deflection of the flexible
element.

5 One group of these detecting methods is based on coupling the cantilever to
another distance sensitive microscope. A combination of the cantilever with a
scanning tunneling microscope is described, for example, in the patent
US-A-4724318. Another approach using an evanescent wave coupling sensor,
also known as scanning near-field optical microscope (SNOM) or scanning
tunneling optical microscope (STOM), is described by Diaspro and Aguilar in:
10 Ultramicroscopy 42-44 (1992), pp. 1668-1670.

15 Another group of detecting methods is based on the well known piezoelectric
or piezoresistive effect. An example is described in: M. Tortonese et al., Appl.
Phys. Lett. 62(8), 1993, pp.834-836. These methods provide detection
schemes in which the deflection detector is integrated in the cantilever.

20 Yet another feasible way of detecting the displacement of the cantilever relies
on capacitance sensing and is known, for example, from Joyce et al., Rev. Sci.
Instr. 62(1991), p. 710, and Göddenhenrich et al., J. Vac. Sci. Technol.
A8(1990), p. 383.

25 It is also possible to use the changes in the resonance frequencies of the
flexible element to measure its bending. The fundamentals of this technique
are known and described for example in the patent US-A-3413573.

The displacement of the flexible element can also be measured by applying
optical methods, such as beam deflection or interferometry. The beam
deflection method makes use of the length of the lever. Usually, a light beam,
25 preferably produced by a laser diode or guided through an optical fiber, is
directed onto the lever. A small deflection of the lever causes a reasonable
change in the reflecting angle and, therefore, results in a deflection of the
reflected light beam that is measured with bicell or other suitable photo
detectors. The beam deflection method is simple and reliable. Interferometric
30 methods are described, for example, by Martin et al., J. Appl. Phys. 61(1987),
p.4723, by Sarid et al., Opt.Lett. 12(1988), p.1057, and by Oshio et al.,
Ultramicroscopy 42-44(1992), pp.310-314.

1 Though it is possible to use one of the two "bimetallic" layers simultaneously
as a chemical sensing layer, in most cases a third, distinct layer acting as a
sensing element is required. This chemical sensing layer does not
necessarily has to be a catalyst, even though a catalyst as chemical sensing
5 layer forms a preferred embodiment of the invention. However, the high
sensitivity of the new sensor makes it possible to exploit even the heat
transfer occurring during ad- or absorption of molecules at the surface of the
sensing layer. Therefore , a layer can be chosen which enables a selective
ad- or absorption of the molecules to be detected. Thus, the term "chemical
10 sensing layer" is used to specify the broader scope of the new sensor.
An ideal catalyst is defined as a substance that increases the rate at which a
chemical reaction approaches equilibrium, without itself becoming
permanently affected by the reaction. The catalyst achieves this enhancement
15 by providing an alternative reaction path, involving different activated
complexes, with a lower activation energy than the uncatalysed reaction
mechanism. A wide range of catalysts for many different chemical reactions is
known. For measurements using the catalytic oxidation of hydrogen,
carbonmonoxide, hydrocarbons and other combustible gases, for example, the
transition metals Pt, Pd, Rh, Ir, or their oxides, or a mixture of those materials
20 are preferably applied. It is possible to provide a surface of the cantilever
with a thin catalyst layer by using known deposition techniques, such as
sputtering, epitaxial methods or electrochemical deposition. The surface of a
deposited film can be further enlarged or roughened by etching with a
suitable chemical agent.
25 As said above, another embodiment of the chemical sensing layer is a
material which enables a chemisorption, i.e. the formation of chemical bonds
between the (surface) molecules of said layer and those molecular species to
be detected. The enthalpy of a chemisorptive process is known to range from
approximately 40 kJ/mol to 400 kJ/mol. An energy transfer in this amount can
30 readily be detected by the new sensor. Suitable materials are, for example,
Ni, Fe, Ag, and Pt. The sensitivity of the new device allows in principle also
the detection of adsorption, the energy of which is ranging from 0.3 kJ/mol to

1 3 kJ/mol, i.e. less than a tenth of the energy found at catalytic reactions or chemisorption.

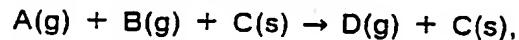
By being able to detect chemisorption and adsorption, the new sensor also forms a valuable device to monitor biochemical processes: The chemical sensing layer is this case is advantageously a Langmuir-Blodgett (LB) film applied to the bimorph cantilever by known methods. Using the defined hydrophilic or hydrophobic surface of the LB film and the affinity between certain molecules, such as proteins and enzymes, it is, thus, possible to tailor a highly specific sensor suitable not only for gas analysis but also for medical test methods, e.g. immunoassay systems. The vast state of art concerning LB films is, for example, referred to in: G.G. Roberts (ed.), Langmuir-Blodgett Films, Plenum, New York, 1990. A method for applying a LB film to the surface of a semiconducting surface is detailed by S. Lee et al., Sensors and Actuators B, 12 (1993), pp.153-154.

15 By changing the temperature, a chemisorption can be reversed, e.g. the chemisorption of hydrogen on nickel or platinum. Many catalytic reactions equally require an initial temperature. The difference in the initial temperature allows to inhibit and suppress undesired reactions. These temperature dependent reactions can be effectively exploited when using the sensor as an analyzing tool. In general, it is more convenient to provide the necessary temperature by heating the chemical sensing layer than by heating the reactants, themselves. As to this reason, the sensor preferably comprises a heating device for the chemical sensing layer. The sensing layer can be heated by a juxtaposed electrical heater, i.e. a thermoelement, or by using electromagnetic radiation.

In a preferred embodiment of the invention, the chemical sensing layer is heated by the same light emitting device which is employed for measuring the deflection of the flexible element by using the above described beam deflection method.

30 The sensitivity of the new device is enhanced by employing a pair of flexible elements only one of which is covered by a chemical sensing layer. This embodiment of the invention has intrinsic reference or calibration properties,

- 1 as both levers bend by the same amount for temperature changes not related to a chemical reaction resulting in a zero difference signal. The desired reaction, however, only effects the bending of the covered lever and is, thus, detected with an enhanced accuracy.
- 5 By combining levers coated with different chemical sensing layers and/or levers held at different temperatures, it is possible to manufacture an artificial nose, able to identify and analyze different gas mixtures. Catalysts specifically sensitized to a single molecule for analyzing purposes readily simplifies the identification of a substance. However, in cases where no such catalyst is available, the levers can be held at different temperatures to obtain the reaction activation energy by evaluating the reaction rate, in particular, if a simple Arrhenius relationship holds between the reaction rate and the temperature. Interferences between several substances may be eliminated by applying multicomponents analysis techniques known per se.
- 10
- 15 In the following, the model (catalytic) reaction



is taken as an example to illustrate the operating principles of the sensor according to the invention. The reaction describes the formation of a gaseous substance D from the two gaseous reactants A and B accelerated by the solid catalyst C left unchanged.

Associated with the reaction is an enthalpy of formation ΔH , giving the amount of heat released to (exothermic reaction) or absorbed from (endothermic reaction) the surrounding per mass unit. In the following, the reaction is assumed to be exothermic, i.e. $\Delta H < 0$. Thus, the formation rate, i.e. the reaction velocity, is corresponding to a certain amount of heat produced per time unit. Except for losses to the surrounding, the heat causes a temperature rise ΔT in the cantilever coated with the catalyst until the formation of heat is balanced by the losses. The change in temperature causes the lever to bend, as it is made of materials with different thermal expansion coefficient. Thus, ΔT corresponds to a deflection of the flexible element from its previous position, which is measured by the means described above. An equal

1 behaviour applies if the reaction is endothermic. In this case, the cooling
induced by the reaction causes the bimorph lever to bend.
By measuring the deflection as such, the sensor presents a highly sensitive
5 detector for the appearance of a certain substance. By using an appropriate
calibration to determine the relation between the reaction velocity and the
amount of deflection, the sensor is useful for quantitative measurements, too.
Due to its sensitivity and small dimensions the sensor can provide a valuable
tool for controlling chemical processes. In particular, it can be used to detect
10 toxic or combustive gases in air, especially to monitor the exhaust gases of
combustion engines and other environmental hazards. Covered by an
appropriate chemical sensing layer, the new sensor is also applicable in
analysing biochemical reactions and as a tool for performing medical tests.

15

DESCRIPTION OF THE DRAWINGS

20

The invention is described in detail below with reference to the following
drawings:

25

FIG. 1 schematically shows an embodiment of the new sensor and an
apparatus for testing it.

FIGs. 2A,B,C show a component of the new sensor in different embodiments.

25

FIG. 3 shows a plot of the deflection of a sensor according to the
invention versus the power of laser radiation.

30

Fig. 4 illustrates the behaviour of the flexible element under operating
conditions.

30

Fig. 4 shows an embodiment of the invention having intrinsic reference
properties.

1 Fig. 5 shows an array of sensors as a one chip device.

EXAMPLES

5.

An embodiment of the new sensor according to the invention is tested by using a conventional atomic force microscope (AFM). FIG. 1 shows a vacuum chamber 1, an inlet 2 for test gas mixtures and an outlet 3 leading to the pumping system (not shown). The chamber 1, further, comprises a holder 4 to mount the flexible element, the cantilever 5 which serves as such flexible element, and a beam deflection system 6 for determining the deflection of the cantilever 5. A light beam 7 is generated by a laser diode 8. In operation, the beam 7 is reflected from the cantilever 5 and the reflected beam 9 is surveilled by a two sectors of a quadrant detector 10. The quadrant detector is operated in the (A-B)/(A+B) mode to normalize for fluctuations in the laser power. The beam deflection system comprises means 11 to determine the deflection of the cantilever 5 using the signals received the detector 10. To demonstrate the operating principle of the new sensor as a calorimeter, a beam-shaped bimorph cantilever as shown in FIGs. 2A,B is employed. The cantilever's base material 21 is Silicon with a thickness of $1.5 \mu\text{m}$ coated by a $0.4 \mu\text{m}$ thick layer 22 of Al using a vacuum evaporation technique. Both layers 21, 22 have thermal expansion coefficients α_1, α_2 which differ significantly as having the values $3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for Si and $25 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for Al. The layers 21, 22, thus, form the desired bimorph or "bimetallic" junction. Using again vacuum evaporation, a 40 nm thick Pt layer 23 is deposited on top of the Al layer to act as catalyst. The overall dimensions of the applied cantilever are: $l=400 \mu\text{m}$, $w=35 \mu\text{m}$, and $t=1.94 \mu\text{m}$. The linearity and the response time of the sensor are tested by varying the output power the laser diode 8 from $400 \mu\text{W}$ to $600 \mu\text{W}$. As shown by FIG. 3, the deflection of the bimorph cantilever relates linear to the heat transfer induced by radiation of the laser diode the power of which ranges from $400 \mu\text{W}$ to $600 \mu\text{W}$. The data further show that an effective heating of the

1 cantilever can be achieved by using the laser radiation of the deflection beam system. Thus, it is possible to heat the chemical sensing layer 23 above the ambient temperature.

5 By measuring the response of the cantilever 5 to a laser pulse of 300 μW , a response time of approximately 1 ms is determined for a device according to the example.

In another example, the new sensor is applied to monitor a chemical reaction. A triangularly shaped cantilever 5 is used as illustrated by FIGs. 2A,C. The cantilever's base material 21 is silicon nitride (SiN), coated by a 0.2 μm thick 10 layer 22 of Al using vacuum evaporation. Using the same technique, again, a layer 23 of Pt is deposited onto the alumina as catalyst. The layer 23 has a thickness of 20 nm. As in the previous example, fine intermediate layers formed by the oxidation of the freshly etched or deposited surface are not taken into account as separate layers. The dimensions (see FIGs. 2A,C) of the 15 cantilever are: $l = 200 \mu\text{m}$, $w = 20 \mu\text{m}$, and $t = 2 \mu\text{m}$ with a force constant of approximately 0.1Nm^{-1} .

Refering to FIGs. 1 and 4, the device is tested by using the reaction:



20 with a reaction enthalpy of 242 kJ/mol, catalyzed by the Pt layer 23. First, the vacuum chamber 1 is pumped to a pressure of 10^{-5} mbar to remove unwanted gaseous residues. Then, the chamber is filled with a mixture of H_2 and O_2 in the correct stoichiometric ratio (2:1) up to a pressure of 2×10^{-2} mbar.

25 Due to the heat production $\Delta Q/\Delta t$ of the reaction at the catalytic surface 23, the temperature of the cantilever 5 rises until the produced heat is balanced by the heat losses $\Delta Q(\text{Loss})/\Delta t$. The temperature rise corresponds to a bending of the cantilever as depicted in FIG. 4. After bending, the laser beam 9 is reflected in a slightly different angle compared to the unbended case.

30 The difference is measured by the detector 10. Under the described conditions, the cantilever was deflected by 150 nm, thus, giving a theoretical

1 detection limit for hydrogen of 10^{-7} mbar, as a deflection of 0.1 nm can still
be detected under optimum conditions.

5 It is further possible to enhance the sensitivity of the sensor by eliminating
some of the background noise by using a device which compensates for
temperature shifts not caused by the catalytic reaction, itself. An example of
such a device with an intrinsic calibration is shown in FIG. 5. It comprises a
second lever 51 almost identical to the first lever 5 lacking, however, a
chemical sensitive layer 23. The deflection of each lever is measured with the
same means 6 as described above (see FIG. 1), additionally comprising means
10 52 to determine the difference between the deflection of both lever 5, 51. By
measuring the deflections of both levers and evaluating their difference, the
background shifts due to changes in temperature and other effects are
diminished.

15 By coupling several sensors (with intrinsic calibration), each sensitized to a
different species A, B, C, D, E, F, and G, as illustrated by FIG. 6, a
multi-component analyzer is realized. Letters A', B', ..., and G' denote the
uncoated reference levers used to eliminate the background noise. Though a
careful choice of the catalysts and temperature conditions has to be made by
a skilled person, the fundamental principles of the device remains unchanged:

20 An analysis of the deflection of each lever or pair of lever gives the amount of
the component for which the lever has been sensitized. Interferences
occurring due to a partial sensitivity of a catalyst for more than one species
can be filtered out by an appropriate mathematical method.

25 As all components (levers, laser diodes, photo detectors, etc.) are producible
on the semiconducting base material (Si), it is readily feasible to manufacture
also large arrays of the sensor on a single-chip basis.

1

CLAIMS

1. A calorimetric sensor, especially a calorimetric gas sensor, comprising a flexible element (5) with at least two layers (21, 22) of materials with different thermal expansion coefficients, one of which is a chemical sensing layer (23), and means (6) for determining the deflection of said flexible element (5).
2. A sensor in accordance with claim 1, comprising at least two layers (21, 22) of materials with different thermal expansion coefficients and at least one chemical sensing layer (23).
3. A sensor in accordance with claim 1, wherein the means (6) for determining the deflection of the flexible element (5) is chosen from a group comprising means for measuring the tunnel current between the flexible element (5) and a probing tip, means for measuring the intensity of an evanescent electro-magnetic wave guided through the flexible element (5), means for determining a piezo-electric/resistive change of the flexible element (5) while bending, means for measuring the capacity between the flexible element (5) and another surface, interferometric means, and beam deflection means.
4. A sensor in accordance with claim 1, comprising means for heating the chemical sensing layer (23).
5. A sensor in accordance with claim 3, wherein the heating means is a resistance heater, or a thermoelement, or an emitter (8) of intensive electromagnetic radiation.
6. A sensor in accordance with claim 1, wherein the chemical sensing layer (23) is a catalytic layer.
7. A sensor in accordance with claim 1, wherein the chemical sensing layer (23) is a catalytic layer comprising a transition metal, or an oxide of said metal, or a combination of those materials.
8. A sensor in accordance with claim 1, wherein the chemical sensing layer (23) comprises an organic material, preferably a Langmuir-Blodgett film of said organic material.

1. 9. A sensor in accordance with claim 1, comprising means for compensating a background deflection of the flexible element (5).
10. A sensor in accordance with claim 9, wherein the compensating means comprises a pair of flexible elements (5, 51) made of identical materials, only one having the chemical sensing layer (23), means (8, 10) for determining the deflections of both flexible elements (5, 51) simultaneously, and further means (52) for determining the difference between said deflections.
11. An array, comprising at least two sensors in accordance with claim 1, wherein each sensor has a different chemical sensing layer (23).
12. An array, comprising at least two sensors in accordance with claim 4 , wherein the chemical sensing layers (23) of said two sensors have different temperatures under operating conditions.

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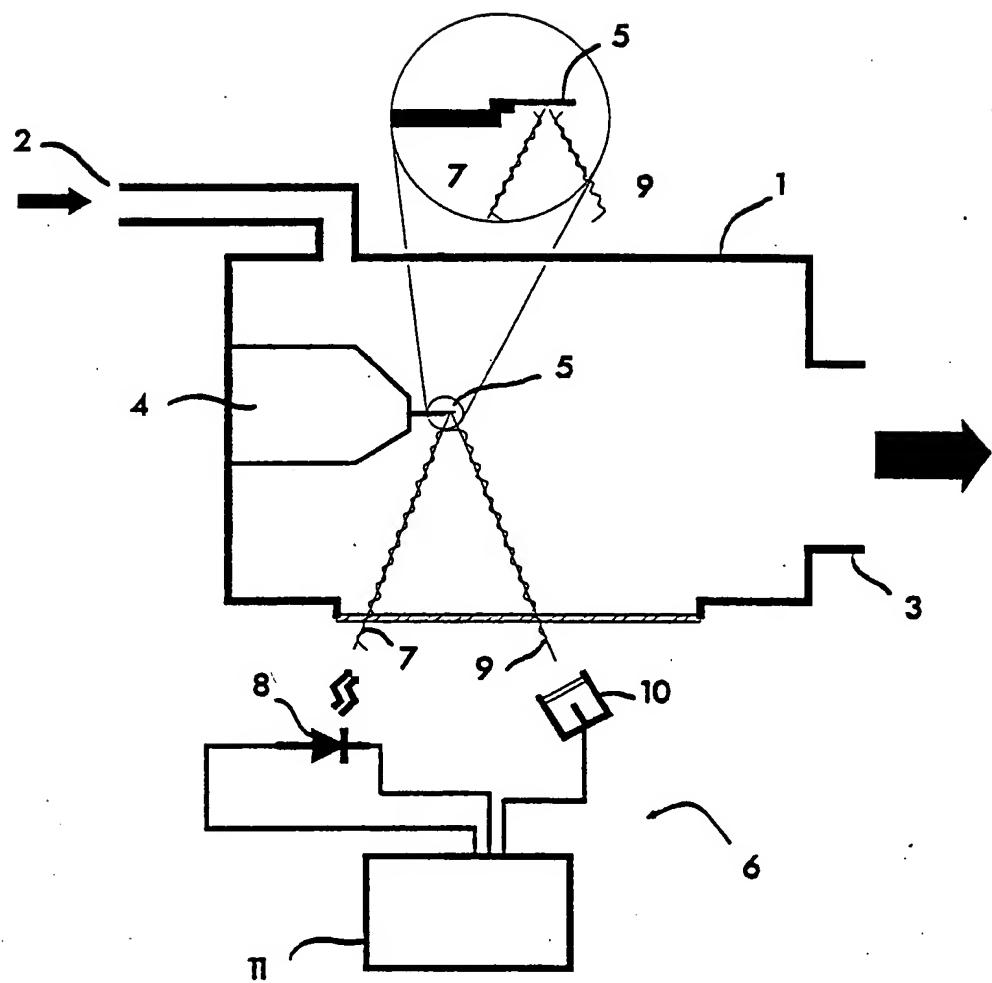


FIG.1

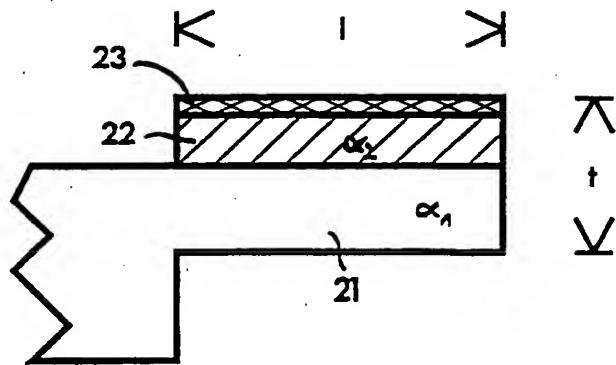


FIG.2A

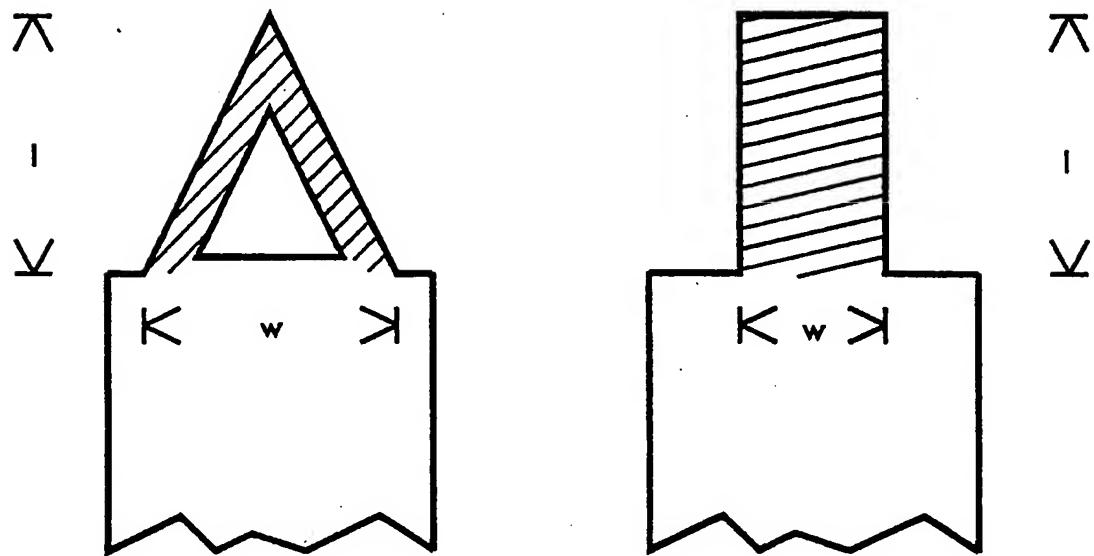


FIG.2C

FIG.2B

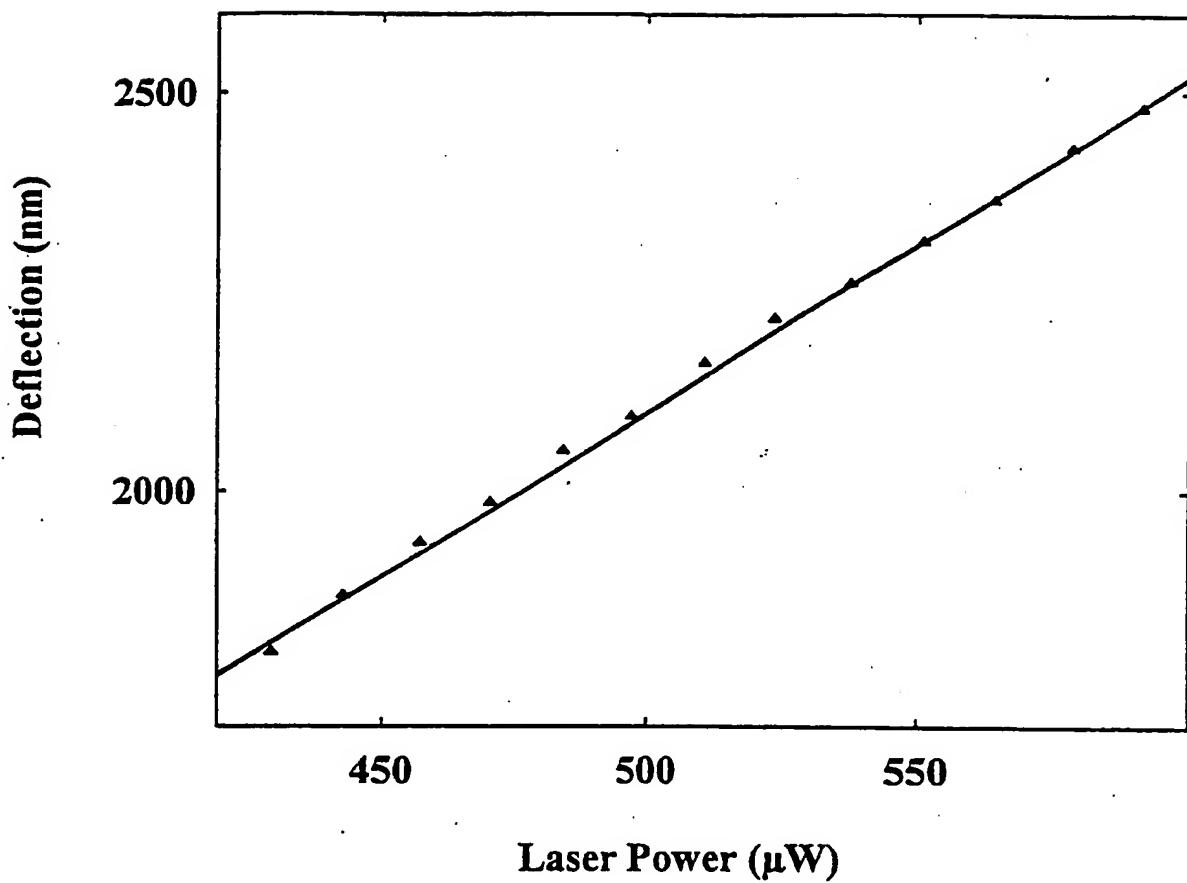


FIG.3

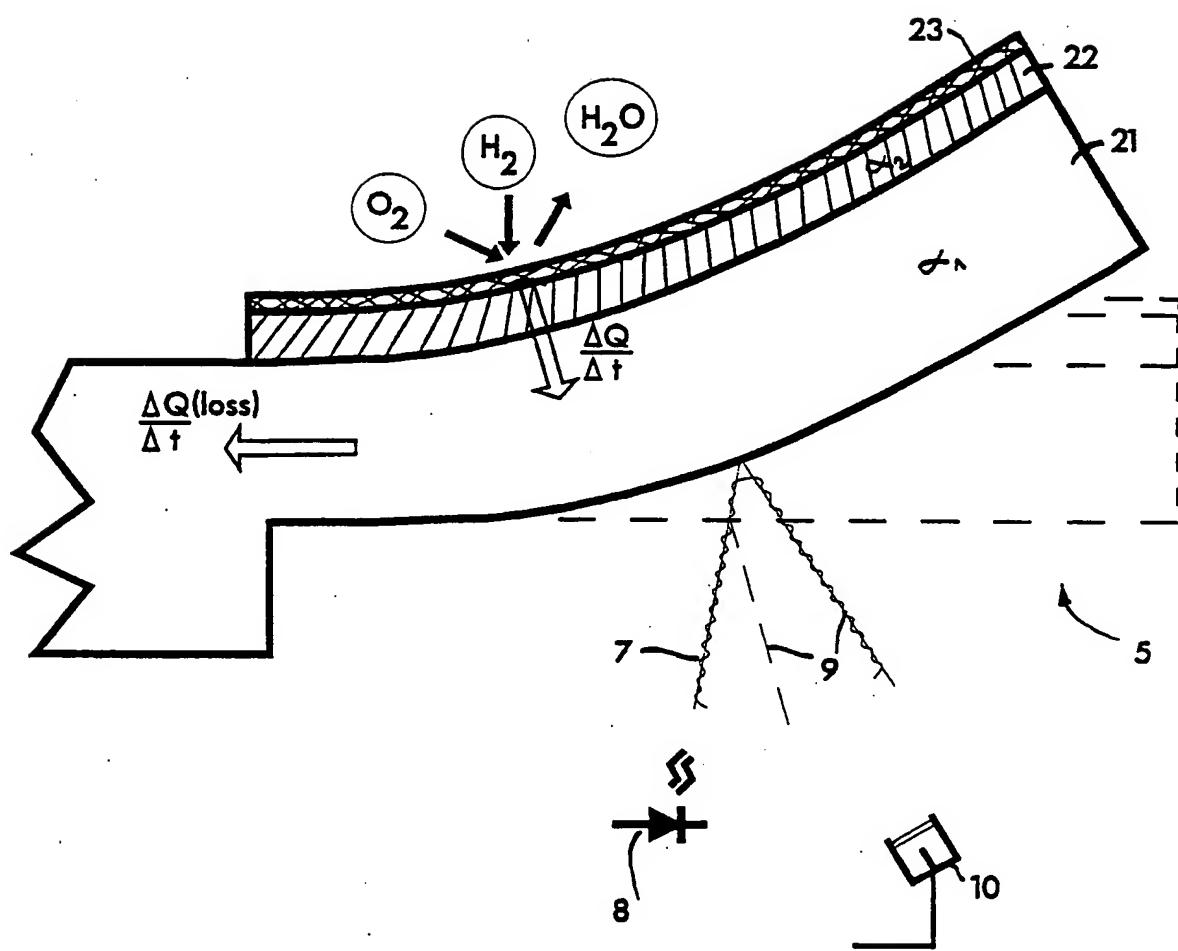


FIG.4

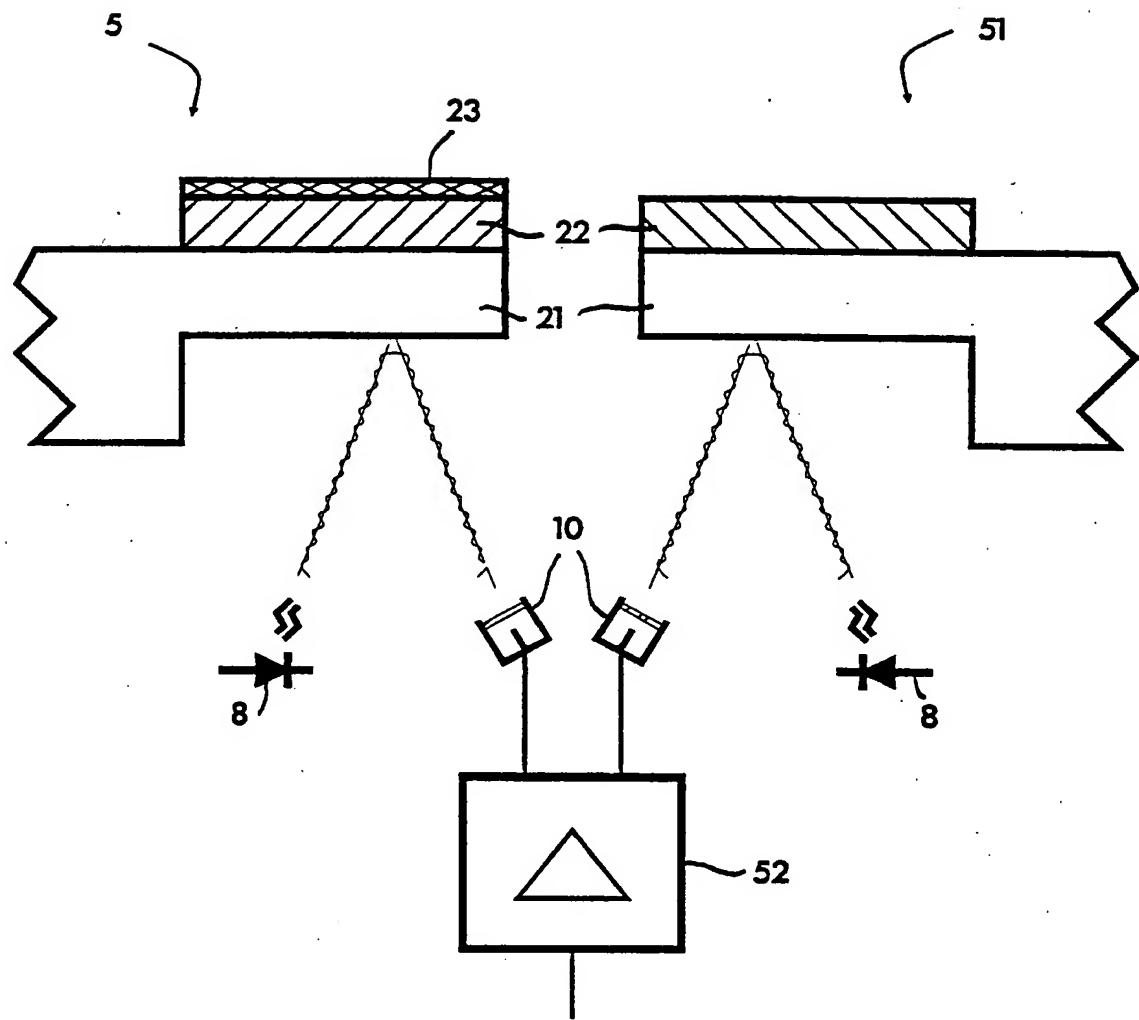


FIG.5

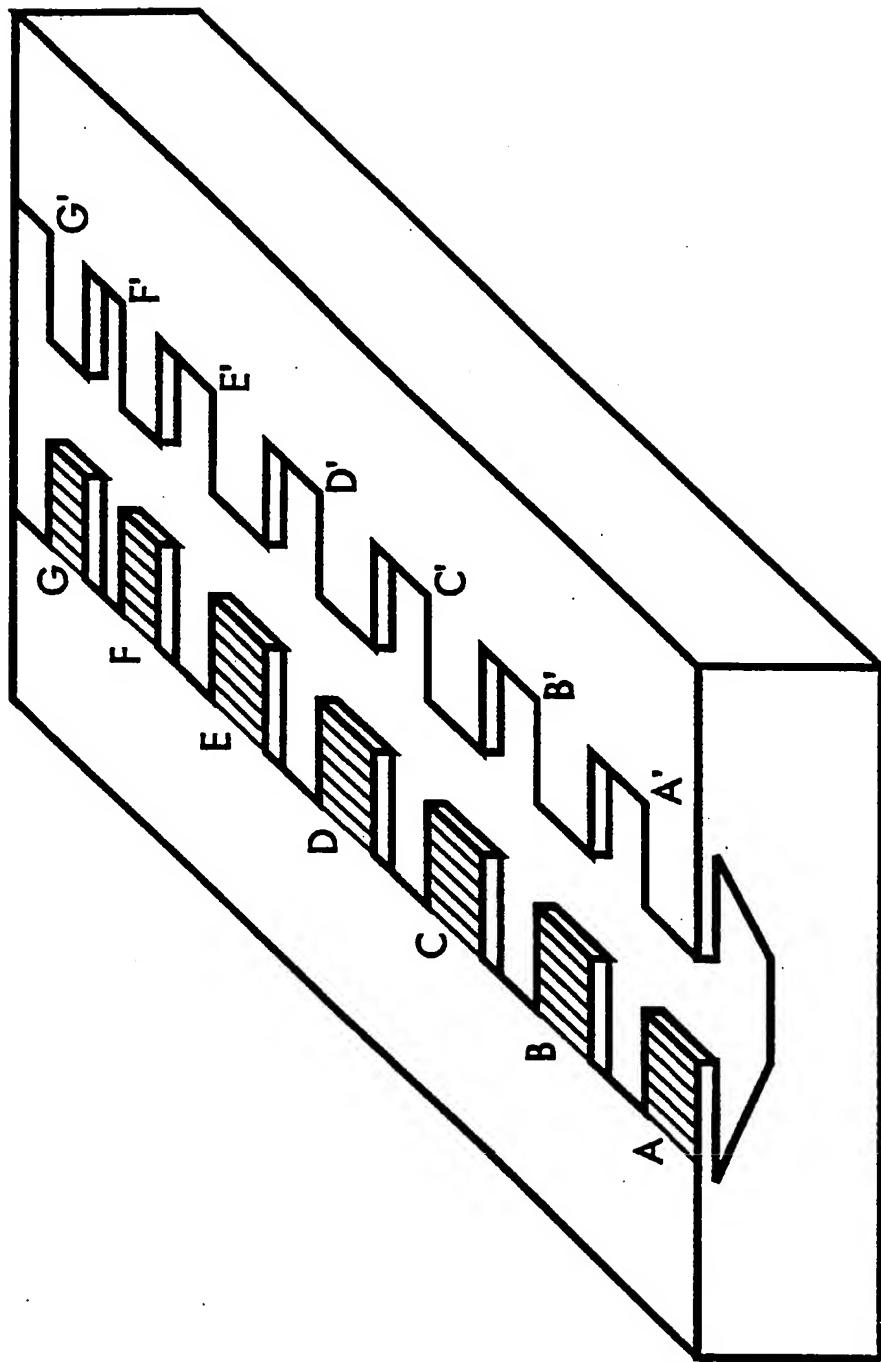


FIG.6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01742

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 G01N25/36 H01H1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 G01B G01N H01H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,C,875 881 (CONCORDIA ELEKTRIZITÄTS-AKTIONESELLSCHAFT) 8 July 1949 see the whole document ---	1-7,9,10
Y	WO,A,89 09477 (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 5 October 1989 see the whole document ---	1-7,9,10
Y	US,A,2 745 721 (C.TIFFANY ; N.J.ENGLEWOOD) 15 May 1956 see especially column 3 ,lines 30-66, fig 1 see the whole document ---	1,2,4-7
Y	US,A,2 881 274 (W.A.RAY) 7 April 1959 see the whole document ---	1,2,4-7
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

1 Date of the actual completion of the international search 14 March 1994	Date of mailing of the international search report 05.04.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Brock, T

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/EP 93/01742

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	FR,A,2 287 698 (DICTAPHONE CORP) 7 May 1976 cited in the application ---	1
A	EP,A,0 511 662 (MATSUSHITA ELECTRIC INDUSTRIAL CO LTD) 4 November 1992 see page 5, line 29 - page 13, line 39; claims 1,4-9; figures 1-9 -----	1,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

PCT/EP 93/01742

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		DE-A,C	2543024	22-04-76
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		US-A-	4068021	10-01-78
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